



Preparation and characterisation of hydrotalcites colloid dispersions suitable for deacidification of paper information carriers

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Abstract

Hydrotalcite samples were prepared in the form of powder and/or sol under different conditions and characterised by various techniques. A suitable system of liquid carriers consisting of perfluoroheptane, isopropanol, and water (PFH-IPA-H₂O) was chosen to apply HTlcs as deacidifying agents on paper. The areas of miscibility and immiscibility in the PFH-IPA-H₂O system were determined at a temperature of 25 °C. The properties of HTlcs dispersed in the prepared solvent were measured. The size of the particles was determined by optical microscopy with image analysis. The average particle size ranges from 1 µm to 2 µm. The settling speed of particles in the prepared colloidal systems was monitored using turbidimetry. Sols in the mixture of solvents had uniformly dispersed particles that settled slowly. The effect of the prepared colloidal HTlcs dispersions on the properties of the paper, specifically the pH of its surface, was also tested. Hydrotalcites in the form of a sol with a ratio of magnesium to aluminium of 5:1 were found to be promising candidates for deacidification. The use of surfactant additives in the preparation of HTlcs did not positively affect the properties of the paper.

Keywords HTlcs · PFH-IPA-H₂O phase diagram · Acidic paper · Deacidification

Introduction

Until the beginning of the nineteenth century, paper was manually made from plant fibres and animal-based sizing agents were used (Blüher and Vogelsanger 2001). In 1805, Moritz introduced the paper using rosin and alum (KAl(SO₄)₂); later aluminium sulphate (Al₂(SO₄)₃), which

made the paper stronger and less sensitive to water. However, the acidic components of the sizing agents, together with the residual reaction components of the sulphate and sulphite pulping process, reduced the pH of the paper to 4.0–4.5 and the paper began to age significantly faster. More than 90% of books from the nineteenth century and 80% from the twentieth century are printed on acidic papers, and extending their life is a global problem (Biermann 1996). The actual degradation of paper material is a permanent chemical process. It is affected by internal factors such as pH, fibre type, presence of lignin and transition metals, decomposition products, and external factors: humidity, temperature, oxygen, ultraviolet (UV) radiation, sulphur and nitrogen oxides, dust, and mechanical damage. Signs of degradation processes are loss of mechanical properties (brittleness), colour change, and reduced legibility (Area and Cheradame 2011).

Currently, several basic types of restoration-deacidification techniques are used. A dispersion of solid particles of MgO in perfluoroheptane (PFH), called the "Book-keeper process" is among the most widely applied deacidification processes. The size of the MgO particles is small (in the range of micrometres), allowing the MgO

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particle to penetrate the paper fibres sheet more easily. The concentration of MgO in the dispersion is about 2.5 g/L (Buchanan et al. 1994). In large-scale processes, PFH is completely recycled. To prevent magnesium oxide particles from clumping in perfluoroheptane, we used polyoxyperfluoroalkanoic acid as a surface-active compound to stabilise the dispersion. This surfactant is completely bound to MgO, which remains in the deacidified material. The water present in the paper ensures the dissolution of MgO as well as the transport of solid particles of MgO into the structure of the paper. By deacidification, the pH value of the paper is increased to a neutral to slightly alkaline range, and an alkaline reserve is created to neutralise the acids produced in the paper during the next ageing. A detailed overview of the mechanism of degradation of cellulose, protection methods, and evaluation methods is provided by Strlič et al. (2005). A more recent review of deacidification techniques can be found in the work of Baty et al. (2010).

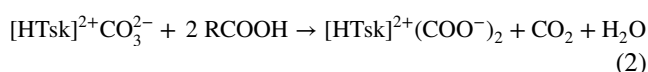
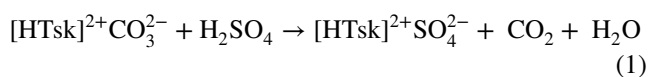
The penetration of deacidifying agents into the structure of paper fibres is the key to the longevity of documents. For solid substances, it is necessary to transform them into a soluble/solvated form and then transport them into a paper volume. The depth of penetration of an effective deacidifying substance depends on the size of the particles (or molecules), the polarity of the solvent or the whole impregnation system, and other technological factors (Fellers et al. 1989).

In this paper, we focus on the stabilisation of cellulose and paper using hydrotalcites (HTs) and hydrotalcite-like substances (HTLcs), respectively. These substances (also called “layered double hydroxides”–LDHs) are widely used as deacidification agents in the field of stabilisation of synthetic polymers (Bart 2006; Bocchini et al. 2008; Wang and Zhang 2004; Xue et al. 2014) where they act as “acid scavengers”. Acid scavengers have an important effect on maintaining melt viscosity during the process and on the long-term stability of the final polymer product (Thürmer 1998). The application of LDHs in binding anionic contaminants from water was also successful (Châtelet et al. 1996; Lambert et al. 1997; Klumpp et al. 2004). HTs or LDHs modified with surfactants improve the properties of polymers and reduce their flammability compared to those of pure polymers. Especially Mg/Al LDHs are coming to the fore not only because of the good self-extinguishing properties resulting from the synergistic effect of Al(OH)₃ and Mg(OH)₂ (Kalali et al. 2015; Li et al. 2016), but also due to improved hydrophobic properties. They can be used, for example, in the protection of wood and materials based on it (Guo et al. 2017). Similar results were also obtained by Wang et al. (2010) by preparing multifunctional Mg/Al LDHs coatings on fibreboards that showed very good self-cleaning, self-extinguishing and hydrophobic properties. Applications for mass industrial stabilisation, deacidification, or preservation

of natural, cellulosic, and renewable cellulosic materials are not described in the available literature.

HTLcs are compounds whose structure contains positively charged layers of mixed hydroxides, between which there are anions necessary for charge compensation, with the general formula $[M^{2+}_{(1-x)}M^{3+x}(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ (Cavani et al. 1991). The most common hydrotalcite contains magnesium in the form of a divalent cation and aluminium in the form of a trivalent cation. Hydroxide (OH⁻) and carbonate (CO₃²⁻) groups are usually present as anions. However, HTLcs are also known to have other cations and anions. Such cations are formed by, e.g. zinc, iron, copper, nickel, chromium, scandium, or cobalt. Carbonate, sulphate, hydroxide, chloride, nitrate, and their mixtures, as well as organic anions such as acetate, benzoate, or terephthalate, can serve as an anion (Cavani et al. 1991; Nishimura et al. 2013). Because of the layered structure, HTLcs should penetrate more easily into the bulk of the porous cellulosic material, especially in the case of nanoparticles, compared to the standard MgO particles used in the deacidification technologies.

The potential for the application of HT as a deacidifying agent also comes from its application as antacids to suppress a burning feeling in the chest or stomach of a human being (Cavani et al. 1991). A standard HT antacid (Mg₆Al₂(OH)₁₆CO₃·4H₂O) has a pH of approximately 9. The first stage of deacidification of aged papers—elimination of H₂SO₄, HSO₃⁻ (residues from the so-called Kraft process of pulp preparation and alum sizing, Biermann 1996) and organic acids (RCOOH—resulting from cellulose degradation processes, Area and Cheradame 2011) is an anion exchange process, with simplified reactions:



where [HTsk] is a double-layered HT skeleton.

The hiding of acid species within the body of HT immediately helps to increase the pH and hinder acid degradation processes.

In the next step of deacidification, aluminium and magnesium hydroxides from the HT skeleton react, forming the corresponding aluminium and magnesium salts. As for aluminium, its tangly chemistry (polycations and polyanions) must be considered (Hem and Roberson 1967), particularly concerning the presence of sulphate anions (Singh 1969). The acidity of Al₂(SO₄)₃ (the pH of the 0.1 M water solution is equal to 3) is compensated by the Mg(OH)₂ (saturated water solution, pH = 10.3) released from HT. Of course, the presence of aluminium cations as a residue of the alum sizing process must be considered. For these reasons, HTs with higher Mg: Al ratio (at least 4) is more

suitable for deacidification than typical hydrotalcite like $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$. This fact is also nicely illustrated by Parashar et al. (2012), who tested the antacid activity of HT with various Mg:Al ratios.

In general, HTlcs are prepared from aqueous solutions by mixing water-soluble magnesium and aluminium salts (in molar ratios of 2:1 to 4:1) with an alkaline solution containing at least a double excess of carbonates and enough alkali so that the pH of the reaction mixture reaches a value of 7 and 10 (Cavani et al. 1991; Nishimura et al. 2013). The size of the particles of the prepared HTlcs can be influenced by reaction conditions such as temperature, mixing speed, rate of addition of reactants and their concentration and pH adjustment of the reaction mixture. (Xantos 2010). Through controlled synthesis, plate-like, needle-like, or spherical morphology of the prepared HTlcs particles can be achieved (Wang et al. 2012).

The application of HTlcs in the form of colloidal dispersions is assumed to stabilise paper carriers of information. A suitable deacidifying colloid system should contain nonpolar, hydrophobic (e.g. PFH), polar, hydrophilic (water) and mild polar (alcohol) solvents/carriers. Water allows better penetration of the hydrotalcite particles into the paper structure and at the same time causes swelling of the fibres and enables the penetration of the active deacidification components into the cellulose wall of the fibres. Isopropanol represents an intermediate that ensures the miscibility of PFH and water, which are otherwise immiscible. However, excessive amounts of isopropanol and water have a negative effect on the paper carriers of information (corrugation), and therefore it is necessary to add them in a small amount as possible. Therefore, it is necessary to know the ternary phase diagram of PFH–isopropanol–water that has not yet been published in the available literature.

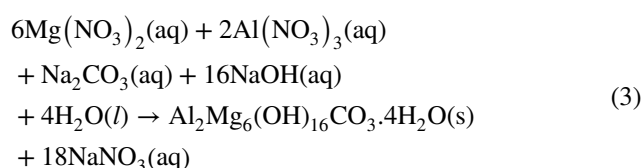
The aim of the work was to prepare hydrotalcites with the desired particle size below 1 μm ; finding a suitable liquid carrier for their application and preliminary experiments to verify their use for the stabilisation and deacidification of acidic paper information carriers.

Experimental

Synthesis of hydrotalcites

The HTlcs were prepared by two precipitation methods: precipitation at low supersaturation and precipitation at high supersaturation. At the low supersaturation method, the crystals of HTlc are better developed, but the particles formed are larger (Cavani et al. 1991).

The HTlcs synthesis was performed according to Eq. (3). The Mg:Al ratio varied from 3:1 to 5:1. In some experiments, chlorides were used instead of nitrate reactants.



Chemicals

$\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ p.a. Lachema; $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ p.a. Lachema; Na_2CO_3 p.a. Lachema; NaOH p.a. Centralchem; $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ p.a. Lachema; $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ p.a. Lachema; Citric acid, anhydrous, p.a. Centralchem; Magnesium stearate, puriss, Sigma-Aldrich; Calgon power powder; Commercial hydrotalcites: HT Sigma-Aldrich; HT-4AV, Kisuma Chemicals.

For the preparation of HTlc, initial solutions with the following concentrations were used: sodium carbonate solution with a concentration of 26.5 g/L; a solution containing magnesium and aluminium ions: 11.3 g/L Mg^{2+} and 4.2 g/L Al^{3+} (for the ratio of Mg:Al = 5:1: 18.8 g/L Mg^{2+}); and a solution of 1 M NaOH.

Precipitation at low supersaturation

A solution containing magnesium and aluminium ions was gradually added to the sodium carbonate solution using a peristaltic pump at a constant rate of 0.6 mL/min under intensive stirring. A constant $\text{pH} = 10 \pm 0.15$ measured with a glass electrode was maintained by adding 1 M NaOH also using a peristaltic pump. The experiment was carried out under laboratory conditions. After the end of the synthesis, the suspension was centrifuged and washed with deionised water until the nitrate ions were washed out, which was verified with Quantofix indicator paper for the nitrate content. The product was dried in an oven at 60 °C.

Precipitation at high supersaturation

1 M NaOH was poured into the Na_2CO_3 solution immediately in such an amount that after synthesis the $\text{pH} = 10$ was reached (the amount was determined in previous experiments). At the same time, the solution containing magnesium and aluminium ions was poured into the prepared mixture. The mixture was stirred intensively for 10 min at a speed of 2500 RPM. The result of this rapid synthesis was a colloidal solution. After removal of nitrates, the product was used directly in the form of a colloidal solution (sol) or was dried and ground. In the following, the samples are designated as A for sols and B for powders.

It should be mentioned that during the preparation of HTlcs from chloride salts, the leaching of chlorides was checked with Quantofix indicator paper for chloride content.

To influence the resulting structure and particle size of hydrotalcites (and thus their properties), several different surfactants were added to the reaction mixture. According to the patent US 2013/0331497A1 (Brod and Glende 2013), surfactants can act as growth inhibitors, e.g. sodium citrate/citric acid, polyphosphates, e.g. Calgon® N. Fatty acids can also be added, e.g. diluted solution of sodium or potassium stearate. The carboxyl groups contained in the stearate will allow each of the precipitated HTlc particles to be coated separately, which should also ensure the deagglomeration properties. In this work, we used citric acid and magnesium stearate in the amount (10–50) wt.% in relation to the amount of hydrotalcite produced. These substances were dissolved in Na₂CO₃ solution. The effect of Na₂CO₃ solution saturated with Calgon powder was also tested.

Characterisation of hydrotalcites

The powdered HTlcs were characterised by XRD (Philips PW1349/30) and DTA (Perkin Elmer 6300—in the range (40–600) °C, heating rate 10 °C/min). After freezing, the sol samples were characterised by SEM on a JEOL 7500F instrument.

Sol samples were characterised by gravimetric analysis. Part of the sample was dried at 105 °C and the water content was determined.

A Leica DM6 M fluorescence microscope was used to measure the approximate particle size of HTlcs in colloidal dispersions. The sample was prepared by dropping a small amount of the shaken solution onto a slide using a micropipette and then covered with a coverslip. The excess liquid was wiped off. A representative part of the sample was found

and a magnification suitable for reading the particle sizes (image analysis by Leica software) was used.

Turbidity Meter Orion AQ3010 ThermoScientific was used to measure turbidimetry. The device used is capable of measuring values up to (1000–1200) NTU (Nephelometric Turbidity Units) (Vinter 2013), only. The sample with higher values of turbidity should be diluted in a defined way. During dilution, the mixed solvent PFH-IPA-H₂O was added in the same ratio as in the prepared sample.

Application of hydrotalcites

Solvents

Isopropanol (IPA), 99%, CentralChem; Perfluoroheptane (PFH) obtained by distillation of the Bookkeepers Deacidification Spray, Preservation Technologies B.V.; and deionised water were used.

Phase diagram of PFH-IPA-H₂O

An emulsion of PFH and water of a predetermined composition was prepared. Subsequently, IPA was added dropwise until the emulsion became clear, when a homogeneous liquid phase was formed from two immiscible liquids (Pandurang et al. 2016; Katusčák et al. 1972).

Preparation of colloidal dispersions

The desired mass concentration was 4.3 g/L of hydrotalcite in the solvent mixture (Jablonský et al. 2013). When preparing colloidal dispersions from powders, the appropriate amount of the sample was mixed with 25 mL of PFH

Table 1 Preparation conditions of HTlcs from nitrate salts, A–sols, B–powders

Sample	Mg:Al ratio	Type of preparation	Addition	Content of the water in the sol
10B	3:1	Low supersaturation		
11B	4:1	Low supersaturation		
13B	5:1	Low supersaturation		
12A	5:1	High supersaturation		95.4% H ₂ O
12B	5:1	High supersaturation		
14A	5:1	High supersaturation	10% citric acid	94.3% H ₂ O
14B	5:1	High supersaturation	10% citric acid	
15A	5:1	High supersaturation	50% citric acid + 10% magnesium stearate	91.6% H ₂ O
15B	5:1	High supersaturation	50% citric acid + 10% magnesium stearate	
16A	5:1	High supersaturation	Calgon	90.0% H ₂ O
16B	5:1	High supersaturation	Calgon	

Table 2 Preparation conditions of HTIcs from chloride salts, A–sols, B–powders

Sample	Mg:Al ratio	Type of preparation	Addition	Content of the water in the sol
17B	3:1	Low supersaturation		
18A	3:1	High supersaturation		93.6% H ₂ O
18B	3:1	High supersaturation		
19A	3:1	High supersaturation	50% citric acid + 10% magnesium stearate	94.0% H ₂ O
19B	3:1	High supersaturation	50% citric acid + 10% magnesium stearate	
20A	3:1	High supersaturation	Calgon	93.7% H ₂ O
20B	3:1	High supersaturation	Calgon	

and 0.2 mL of water (a request for a minimum amount of water in the resulting solution). Subsequently, the calculated amount of IPA was added to create a homogeneous solution of PFH-IPA-H₂O with dispersed solid HT particles. When preparing the sol dispersions, the appropriate amount of PFH and IPA was added according to the measured amount of water in it (Tables 1 and 2).

Testing paper

NOVO wood-free paper–paper testing for paper deacidification, recommended by the German Institute for Standardisation DIN for the quality control of deacidification processes (ISO 18344); wood-free, acidic, resin bonded with alum, OBA-free, surface pH = 3.92, produced by KLUG-CONSERVATION.

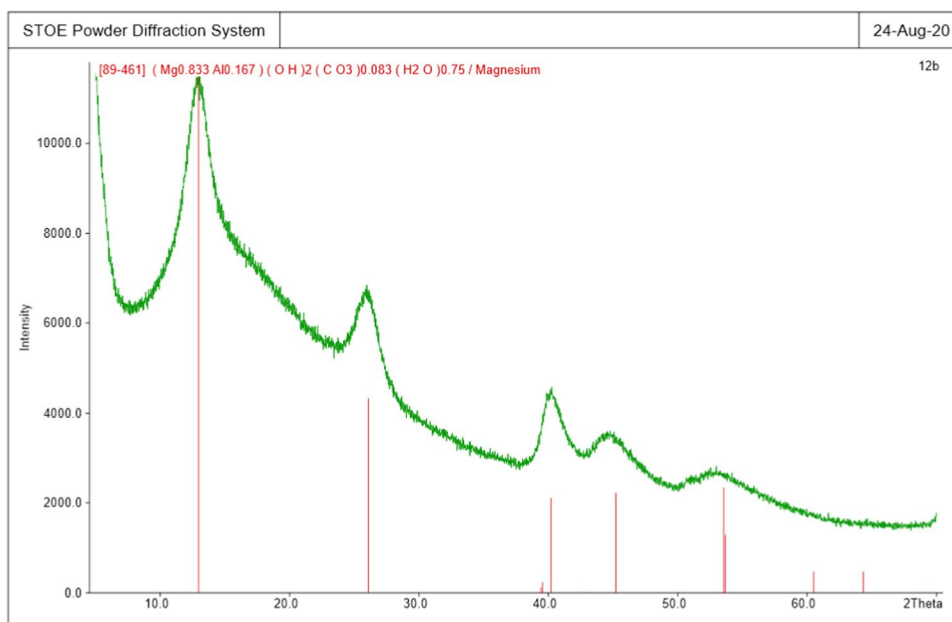
Deacidification of acidic papers

A strip of test paper was immersed in the prepared colloidal dispersion. Subsequently, the closed tube/bottle was placed on a Promax 1020 shaker, Heidolph (10 min, 142 RPM). After being removed from the system, the samples were freely dried on sieves. The surface pH was determined in modified acidic paper samples according to the standard T 529 om-04 Surface pH measurement of paper (Tappi 2004). The resulting value is the average value of at least three measurements.

Results and discussion

Synthesis and characterisation of hydrotalcites

Two series of HTIc samples were prepared: from nitrates (Table 1) and chlorides (Table 2). The preparation conditions are also listed in the tables.

Fig. 1 Powder X-ray diffraction of sample 12B (Mg:Al = 5:1; high supersaturation)

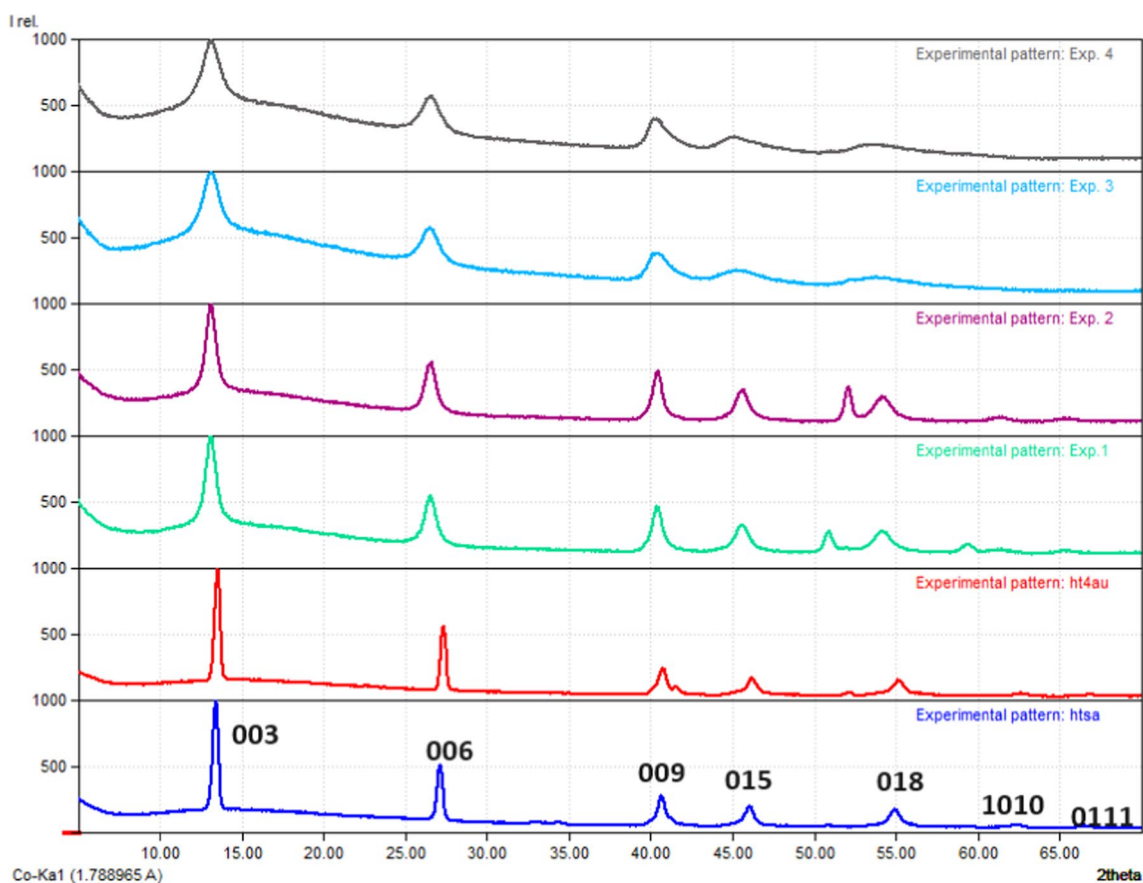


Fig. 2 Comparison of the X-ray records of prepared hydrotalcites with those of commercial ones. (htsa, ht4au): commercial hydrotalcites; (exp. 1, exp. 2): hydrotalcites prepared by slow mixing; (exp. 3, exp. 4): hydrotalcites prepared by rapid mixing

Figure 1 shows a typical XRD record of the prepared hydrotalcites. A comparison of the XRD records prepared at high and low supersaturation together with the commercial hydrotalcite XRD records is shown in Fig. 2. All

of the prepared compounds have a hydrotalcite structure. As expected, hydrotalcites prepared at high supersaturation show a higher proportion of amorphous phase, which agrees with the literature (Cavani et al. 1991; Nishimura

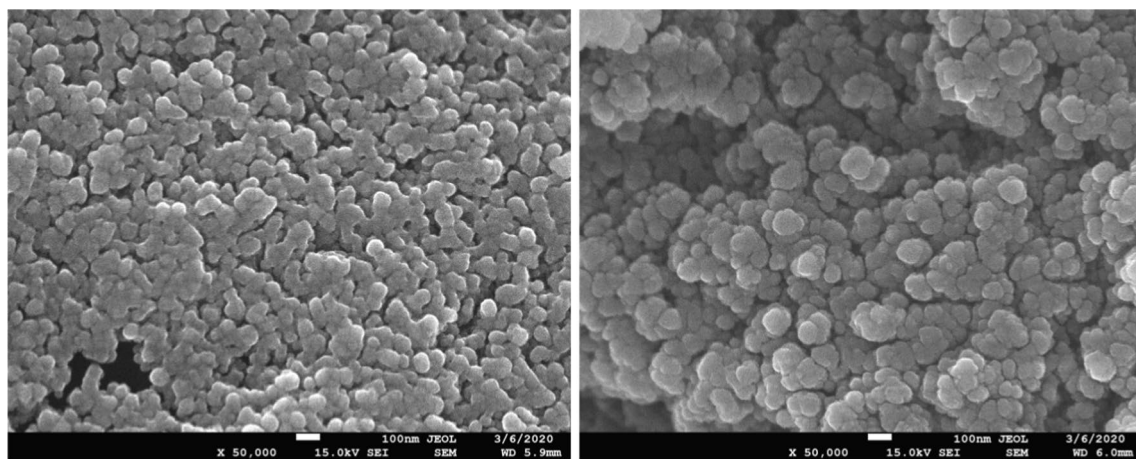


Fig. 3 Comparison of SEM images of prepared hydrotalcites with a ratio of Mg: Al=3:1 (left) and 5:1 (right)

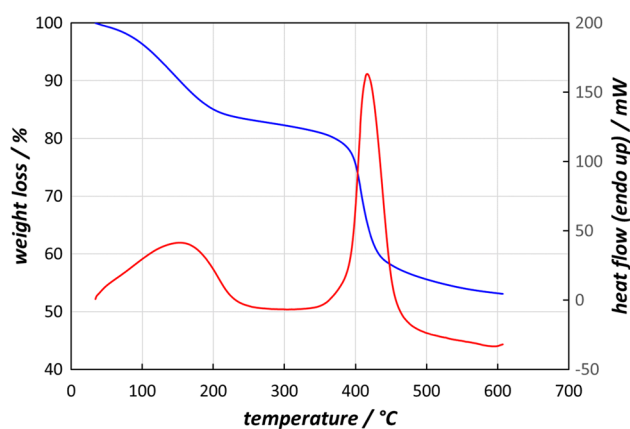


Fig. 4 DTA record of sample 14B

et al. 2013). It should be noted that, because of the preparation of the smallest particles possible, the ageing of the suspension was omitted during the preparation. The ageing improves the crystallinity of the obtained substance, but at the same time increases the size of the particles—the so-called Ostwald ripening (Ostwald 1896, 1897). The comparison of SEM images of prepared hydrotalcites with magnesium to aluminium ratios of 3:1 and 5:1 is shown in Fig. 3. The morphology is very similar, without significant differences, agglomerations of particles smaller than 100 nm are formed. The particle sizes were determined by statistical dimensional analysis for a ratio of Mg: Al = 3:1 (75 ± 9) nm and for a ratio Mg: Al = 5:1 (85 ± 11) nm.

The DTA record of sample 14B is shown in Fig. 4. Hydrotalcite dehydration occurs at the temperatures up to 300 °C (Cavani et al. 1991; Nishimura et al. 2013). In the prepared samples, weight loss ranged from (12.6–15.5)%, which is very well in line with the theoretical value based on the HT formula described in Eq. (3) (12.5%). At temperatures above 300 °C, calcination of the sample occurs (sometimes in two stages (Cavani et al. 1991). The enthalpy of this endothermic step is almost independent of the ratio of magnesium and aluminium in hydrotalcite. In the prepared samples, the enthalpy of this process decreased by approximately 12%, only when the HT ratio was changed from 3:1 to 5:1. It agrees with the enthalpies of the reactions that take place at the calcination, whose values are very close. Therefore, as the magnesium content increases, the enthalpy change in calcination will be smaller, but not significantly, according to Eqs. (4, 5) (HSC Chemistry 2002).



$$\rightarrow \Delta_r H^\theta(400^\circ \text{C}) = 51.62 \text{ kJ/mol} \quad (4)$$



$$\rightarrow \Delta_r H^\theta(400^\circ \text{C}) = 59.65 \text{ kJ/mol} \quad (5)$$

Application of hydrotalcites

Within the application of prepared hydrotalcites, we focus on several aspects: (i) preparation of colloidal dispersions; (ii) construction of the PFH-IPA- H_2O phase diagram; (iii) characterisation of the resulting colloidal dispersions (turbidimetry, particle size); (iv) modification of the paper by colloidal dispersions and change in the surface pH of the paper.

Preparation of colloidal dispersions

Samples in the form of a sol (labelled A) were initially mixed with a nonpolar solvent—pure PFH. Sol did not dissolve; it stuck to the walls of the flask and floated in larger clumps on the surface. The use of additives during preparation had no noticeable effect. As IPA was gradually added to the system, the clusters dispersed. The presence of surfactant additives had a negative effect on the dispersion of particles (the samples with the combined addition of citric acid and magnesium stearate had the worst dispersion).

When samples of powdered hydrotalcites (labelled B) were added to the nonpolar solvent, the powder quickly settled to the bottom. The samples without surface additives settled the fastest, and the samples with the combined addition of citric acid and magnesium stearate settled the

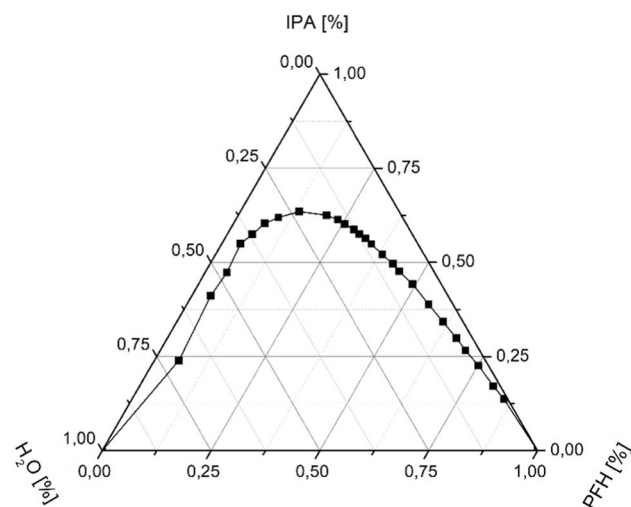


Fig. 5 Phase diagram of a PFH-IPA- H_2O system at a temperature of 25 °C (v/v%)

Table 3 Particle size of powder and sol hydrotalcites in the colloidal mixture PFH-IPA-H₂O-HTlc

Samples from nitrate salts	Particle size (μm)	Samples from chloride salts	Particle size (μm)
11B	1.52 ± 0.15	17B	1.20 ± 0.09
12A	1.54 ± 0.09	18A	1.31 ± 0.15
12B	1.94 ± 0.31	18B	1.59 ± 0.14
13B	1.75 ± 0.15	19A	1.47 ± 0.14
14A	1.12 ± 0.11	19B	1.51 ± 0.21
14B	1.61 ± 0.10	20A	1.47 ± 0.13
15A	1.63 ± 0.23	20B	2.22 ± 0.14
15B	1.41 ± 0.12		
16A	1.64 ± 0.06		
16B	1.38 ± 0.07		

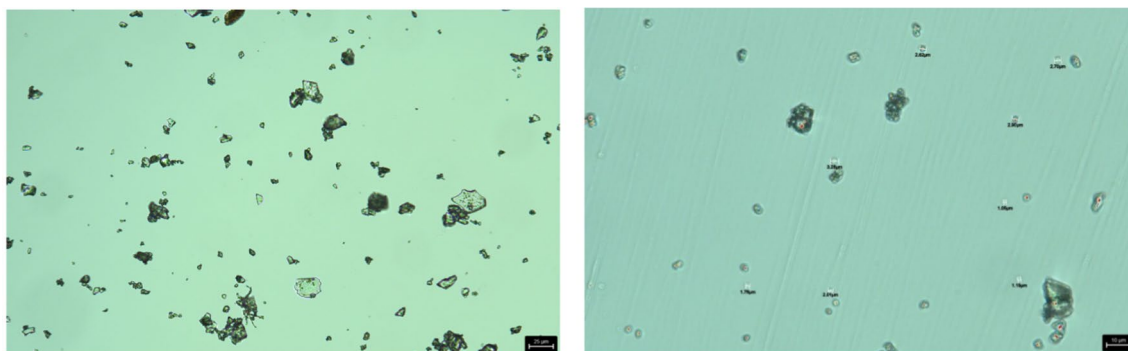
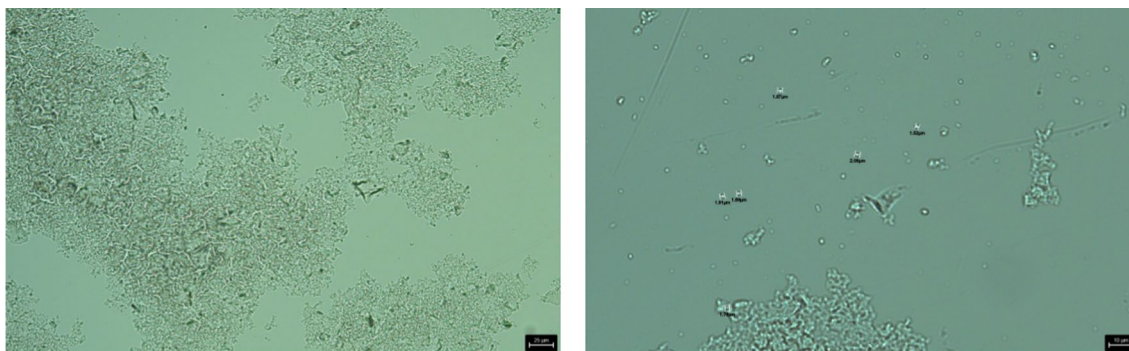
slowest. Colloidal dispersions prepared in this way were not suitable for paper application. Because water causes better penetration of the hydrotalcite particles into the paper structure and swelling of the fibres, allowing better penetration of active deacidification components into the cell wall of the fibres, the addition of water to the system was tested.

Based on these findings, we focus on the construction of the PFH-IPA-H₂O phase diagram (Fig. 5) as a promising carrier of HTlc particles. Isopropanol served as an auxiliary component in the given system, which enabled the formation of a homogeneous liquid phase containing water and PFH. From this, a composition of homogeneous liquid mixture can be read, i.e. when this mixture can be used as a carrier for HTlc.

Characterisation of colloidal dispersions

The particle sizes present in the colloidal PFH-IPA-H₂O-HT dispersions prepared were measured by optical microscopy. The resulting average values of six parallel measurements are summarised in Table 3. The average dimensions of the particles range from 1 μm to 2 μm, except for sample 20B, where the values increased even above the 2 μm.

There were noticeable differences in the behaviour of the sol and powder form of the sample. The sols formed a continuous film, whereas the powders formed regularly dispersed particles on the glass surface. As an example, Figs. 6 and 7 compared the powder and sol of sample 12B. The powdered hydrotalcite clumps into smaller aggregates (Fig. 6), while it formed an almost continuous single layer in sol form (Fig. 7).

**Fig. 6** Microscopic image of a 12B hydrotalcite powder sample. At the bottom of the picture are the 25 μm (left) and 10 μm (right) scales**Fig. 7** Microscopic image of a 12A hydrotalcite sol sample. At the bottom of the picture are the 25 μm (left) and 10 μm (right) scales

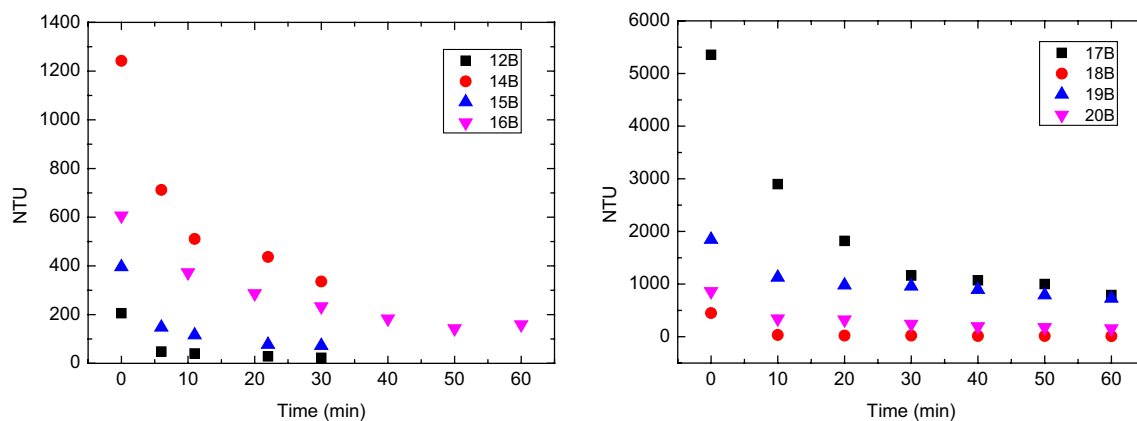


Fig. 8 The course of deposition of sample particles in a mixture of solvents. Samples (left) with a ratio of Mg:Al=5:1 (12B, 14B, 15B, 16B); Samples (right) with a ratio of Mg:Al=3:1 (17B, 18B, 19B, 20B)

As the next step, the stability of the prepared colloidal dispersions was determined; that is, the sedimentation rate of the solid particles, using turbidimetry. Figure 8 shows the turbidimetry results measured for powder samples in a mixed solvent. For comparison, pure PFH has a value of 2.44 NTU.

The settling time of the powder samples in the solvent mixture was around 60 min for samples with the 3:1 ratio of magnesium to aluminium (Fig. 8, right), while the powders of the samples with the 5:1 ratio settled much faster in 30 min (Fig. 8, left). From the effect of the surfactant additives used, it can be seen that the saturated solution of Calgon and the mixture of citric acid and magnesium stearate only slightly reduce the rate of particle settling. If only citric acid was used as an additive, the settling rate was significantly reduced. A similar dependence is shown in Fig. 8 (right), where sample 17B, which was prepared without added surfactant, had the lowest settling speed, but clearly had the smallest particles in the colloidal suspension (Table 3) and therefore probably lasted the longest in levitation.

The turbidity values of the sol samples increased with time. This is due to the very slow settling of the sol particles. During the measurement, the turbidimeter measured the thickening sol mixture because it has formed a larger part of the sample volume (Fig. 9). Therefore, the turbidimetry results of the sol samples are not reliable.

Application of colloidal hydrotalcite dispersions for modification/deacidification of paper

The aim of our research has been to test the suitability of paper deacidification with the above-designed system and, on the basis of the results obtained, to select prepared HTIcs suitable for further investigation. First, the amount of HT

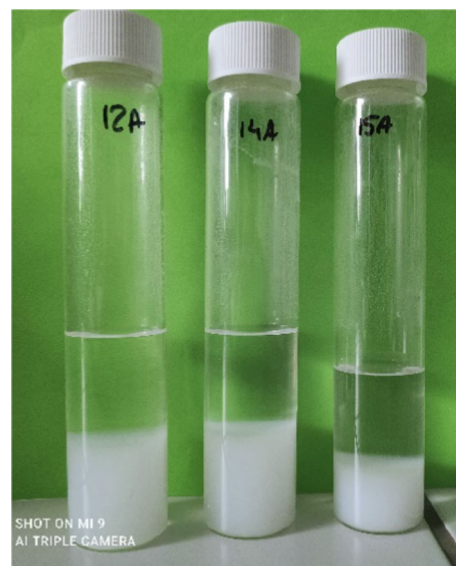


Fig. 9 Samples of sols 12A, 14A and 15A after 50 min of settle in IPA + PFH + H₂O solution

applied to the paper was determined, which was estimated by the difference in the magnesium content in the ash from the modified and original paper that was analysed by ICP-OES. The amount of HT applied was in the range (0.7–1.2) g/m². When HT was prepared by a combination of surfactants (citric acid + magnesium stearate), the deposition of HT on the paper surface was not uniform. This agrees with the negative effect of these surfactants on the particle dispersion, as discussed in the manuscript.

The resulting pH after the application of HT, together with detailed information, is shown in Table 4. The surface pH values of the modified papers were usually in the acid range. In some cases, the pH values were ≥ 6 which are

Table 4 Composition of modification systems with hydrotalcites and pH of the surface of modified samples

Sample	m_h [g]	c_h [g/L]	φ_{PFH} [%]	φ_{H_2O} [%]	φ_{IPA} [%]	pH
11B	0.1265	4.5	89.61	0.72	9.68	5.1
12A	0.1203	4.3	33.20	8.90	57.90	6.4
12B	0.1224	4.4	90.25	0.72	9.03	7
13B	0.1221	4.4	90.25	0.72	9.03	5.8
14A	0.1205	4.3	37.90	7.10	55.00	6.3
14B	0.1206	4.4	90.25	0.72	9.03	5.9
15A	0.1131	4.1	50.40	4.70	44.90	6.4
15B	0.1229	4.5	90.58	0.72	8.70	5.7
16A	0.1203	4.3	62.10	3.90	33.90	5.7
16B	0.1213	4.3	89.00	0.70	10.30	4.3
17B	0.1191	4.2	89.00	0.70	10.30	5.6
18A	0.1208	4.3	46.40	6.40	47.10	5.5
18B	0.1201	4.3	89.00	0.70	10.30	4.6
19A	0.1204	4.3	46.10	6.80	47.10	4.9
19B	0.1210	4.3	89.00	0.70	10.30	6
20A	0.1204	4.3	46.40	6.40	47.10	5.2
20B	0.1207	4.3	89.00	0.70	10.30	5.4

The pH values ≥ 6 which are promising values for the deacidification of acidic papers are highlighted in bold

*16B–water did not build up in the paper

m_h –weight of applied hydrotalcite; c_h –mass concentration of hydrotalcite in the ternary solution PFH-IPA- H_2O ; φ –v/v%

promising values for the deacidification of acidic papers, the pH of which is usually around 4 (Hubbe et al. 2017). The use of sols appears to be a more suitable form of application. Of course, the Mg:Al ratio also plays a role in the deacidification. As shown in Table 4, pH > 6 was achieved only at a ratio of 5:1. This is logical because there is a higher amount of basic magnesium cation. The aluminium cation in the paper acts as an acidic component, and its amount would be advisable to minimise. Hydrotalcite, because of its ion-exchange properties, should allow to remove some of the sulphates from the paper. However, we are still studying this effect. Therefore, on the current results, we assume that a higher ratio of Mg:Al is more suitable. The problem is the viscosity of the relevant dispersion and the high proportion of water (which ranges from (90–96)% by weight to the weight of the prepared sol). The viscosity can cause problems when applied to the paper. A high water content obviously increases the content of isopropanol required as an intermediate. In the case of sols, the system contained (45–58) v/v% of isopropanol, which can be considered as a high proportion. Isopropanol can cause seal damage, ink melting, etc.

According to preliminary results, the use of surfactant additives in the preparation of HTlcs does not positively affect the surface pH of the paper.

Generally, the results presented in this work provide a basis for further research of the paper on deacidification using the hydrotalcites identified in this work.

Conclusions

Hydrotalcite samples were prepared in the form of powder and/or sol under different conditions, and characterisation was carried out. A suitable system was chosen to apply hydrotalcites to the paper, and the areas of miscibility and immiscibility in the PFH-IPA- H_2O system were determined at a temperature of 25 °C.

The properties of HTlcs dispersed in a mixture of non-polar (perfluoroheptane), polar (water), and mild polar (isopropanol) were measured. The size of the particles was determined by optical microscopy with image analysis. The average particle size ranged from 1 μm to 2 μm . The settling speed of particles in the prepared colloidal systems was monitored using turbidimetry. Sols in the mixture of solvents had uniformly dispersed particles that settled slowly. The system appears to be stable. However, the viscosity of the dispersions and the high content of water in them (which ranges from (90–96) wt.%) can be a problem. As the water content increases, the required amount of isopropanol also increases significantly. Isopropanol can cause damage to seals, ink melting, etc. The solution

would be to reduce the amount of water in the prepared sol, which is the subject of further research.

The effect of the prepared colloidal HTlcs dispersions on the properties of the paper, specifically on the pH of its surface, was also tested. Hydrotalcites in sol form of sol with a ratio of magnesium to aluminium of 5:1 appear to be promising. The use of surfactant additives in the preparation of HTlcs did not positively affect the properties of the paper.

The results obtained show a promising basis for further study of the use of hydrotalcites in the deacidification processes of the paper. One of the tasks of future research is to reduce the water content in the sol. It can be achieved, e.g. by washing the prepared sol with isopropanol instead of water. At the same time, the reduced water content will allow the content of hydrotalcite particles to increase in the mixture. As a result of a higher concentration of HTlc, the synergistic effect of its alkalinity and ion-exchange properties can also become more significant.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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